Applied Surface Science Division
Room 204 - Session AS+NS+SA-WeM
Beyond Traditional Surface Analysis

Moderators: Mark Engelhard, EMSL, Environmental Molecular Sciences Laboratory, Kathryn Lloyd, DuPont

8:00am **AS+NS+SA-WeM-1 Solar Wind Interaction with Carbonate Deposits on Asteroid (1) Ceres' Surface: The Role of Surface Analysis in Laboratory Planetary Science***, **Catherine Dukes**, G Rodriguez Lopez, C Bu,* University of Virginia

Bright deposits of anhydrous carbonates across the dark background of dwarf-planet Ceres have been identified by Dawn's VIR spectrometer with a composition that varies from natrite with minor amounts of ammonium bicarbonate within the Cerealia and Vinalia Faculae to magnesite, calcite, and dolomite in other high-albedo regions [1]. These deposits are expected to derive from the aqueous alteration of volatile-containing silicates, forming a viscous brine below Ceres' solid crust. Hydrated salts from this reservoir are deposited on the planetary surface by extrusion through vents or co-ejected by jets of sub-surface water ice. Water loss in the material occurs with exposure to the low pressure environment on Ceres' surface as a function of exposure time, even at temperatures < 240 K [2].

Unprotected from the impacts of solar particles, cosmic rays, and meteorites, anhydrous salts undergo chemical and physical change (space weathering), which can be remotely identified by optical reflectance. The effect of solar-wind ions on carbonates can be simulated in the laboratory, and the correlation between surface composition and morphology with optical change can be used to infer physical processes occurring on airless planetary bodies. We investigate the stability of carbonates and measure systematic darkening with 4 keV He-ion fluence, a potential geologic chronometer for Ceres' bright deposits.

Carbonate powders are pressed into pellets, then introduced into vacuum (10^{-9} Torr) and cooled to ~110/200 K.

An external-beam from an FT-IR is used to perform *in-vacuo* reflectance measurement. Spectra were acquired at varied fluence, equivalent to solar irradiation of ~300 - 30,000 years at 2.8 A.U. Changes in surface composition and molecular chemistry were investigated by *in-situ* X-ray photoelectron spectroscopy (XPS).

Blueish luminescence of sodium carbonates with He^+ is observed. Vis-NIR darkening (~80%) of natrite (Na_2CO_3)occurs after 10^{18} He cm^{-2}, with reddening of the visible spectral slope. Similar darkening is noted for 1.3 - 5 µm, along with attenuation of carbonate overtones. Concomitant XPS measurement shows a reduction of carbon and oxygen, with enhancement of sodium. Exposure of the darkened sample to 10,000 L H_2O-vapor results in brightening to > 80%.

Ion-induced darkening of Ceres' natrite deposits is expected to occur on a time-scale of 100 - 1000 years, and can be reversed by exposure to water vapor. For deposits of varied albedo, this suggests that the brightest areas are the most recent deposits or the most recently exposed to water.

[1] DeSantis et al. (2016) Nature 536, 54-57

[2] Bu et al. (2017) Icarus doi.org/10.1016/j.icarus.2017.12.036

8:20am **AS+NS+SA-WeM-2 Looking Deeper and Smaller: Enhancing XPS by Hard X-ray Probes and High-resolution Imaging***, **Olivier Renault**,* CEA/LETI-University Grenoble Alpes, France*; C Zborowski,* University of Southern Denmark, Denmark*; J Rueff,* Synchrotron SOLEIL, L'orme des Merisiers, France*; Y Yamashita, S Ueda,* NIMS, Japan*; G Grenet,* Lyon Institute of Nanotechnology, France*; S Tougaard,* University of Southern Denmark, Denmark

X-ray photoelectron spectroscopy (XPS) has become a mature technique with a widespread use spanning from fundamental research to R&D labs. In parallel, the intrinsic complexity of materials and systems to be analyzed by XPS has increased. Some of the limitation of XPS are of concern if a non-destructive, non-invasive analytical protocol is the key issue. These are, especially, the poor lateral resolution and the poor bulk sensitivity, making impossible the analysis of microscopic features and buried interfaces in a reliable way.

In this contribution, we review the capabilities of current and novel techniques to get into: (i) high lateral resolution and quantitative micro-analysis using spectroscopic imaging implemented by X-ray PhotoElectron Emission Microscopy (XPEEM); (ii) high depth sensitivity offered by Hard X-ray Photoelectron Spectroscopy (HAXPES), coupled or not with inelastic background analysis to futher enhance information depth up to nearly 100 nm.

We will highlight the capabilities of each techniques by different practical examples in the field of 2D materials [1] and device technology [2, 3], emphasizing particularly the perspectives offered by novel laboratory hard X-ray sources [4].

[1] H. Kim, O. Renault et al., Physical Review B, 2016. 94(8): p. 081401.

[2] P. Risterucci, O. Renault et al., Applied Surface Science, 2017, 402: p. 78-85.

[3] C. Zborowski, et al., Applied Surface Science, 2018. 432(Part A): p. 60-70.

[4] O. Renault, E. Martinez, et al., Surf. Interface Anal. 2018 (in press).

8:40am **AS+NS+SA-WeM-3 Reenvisioning Amphiphilicity: Translating Cell Membrane Design Principles to Synthetic 2D Materials***, **Shelley Claridge**,* Purdue University **INVITED**

2D materials such as graphene exhibit unique electronic and mechanical properties that promise substantial advantages in applications ranging from nanoelectronics to human health. Such interfaces are often functionalized noncovalently with lying-down phases of functional molecules to avoid disrupting electronic structure within the basal plane. Interfacial structures have commonly been characterized down to sub-nm scales using scanning probe techniques such as STM, either in vacuum, or at a solid-liquid interface with a nonpolar liquid (e.g. octadecene). However, molecules used in this approach are often structurally similar to amphiphiles such as fatty acids and phospholipids found in biological cell membranes, suggesting possible utility in *aqueous* environments. At the same time, the overall surface chemistry is strikingly different than that of the cell membrane -- in essence, the surface chemistry is that of a repeating cross-section of a lipid bilayer, with both hydrophilic and hydrophobic components exposed, forming a striped amphiphilic structure with sub-10-nm periodicity.

As 2D materials are integrated into hybrid materials and devices, this noncovalent amphiphilic interfacial structure raises two classes of significant questions requiring interfacial analysis: ***(1) How do noncovalent lying-down ligand layers respond to solution or thermal processing?*** What are the best ways to probe controlled *disordering* across scales from nm to mm at an interface with a polar liquid? If ligand dynamics vary with structure, to what extent can design principles from the cell membrane be invoked to control chemical functionality and reactions at the interface? ***(2) Can noncovalently-adsorbed layers be patterned to template further interactions with the environment?*** Lying-down phases of phospholipids and fatty acids present 1-nm-wide stripes of ordered chemical functional groups, suggesting the possibility of controlling processes such as crystallization, phase segregation, or analyte binding. We examine these questions, again developing approaches to characterize interface structure across the range of relevant length scales, and invoking structural design principles from the cell membrane.

9:20am **AS+NS+SA-WeM-5 Microstructural Effects on Surface Potential of Amorphous Solid Water***, **Caixia Bu**, C Dukes,* University of Virginia

Amorphous solid water (ASW) formed by vapor deposition on substrates <~130 K is of interest for its abundance in Earth's upper atmosphere, icy planetary bodies, and throughout the interstellar medium, as well as its use as model material in many disciplines. Two crucial characteristics of ASW are a self-induced negative surface potential and formation of nanopores [1]. Here, we examine the role of microstructure, including nanopores, on the spontaneous surface potential of ASW, and describe the complementary experimental techniques used, which have application for other microporous solids.

ASW films were deposited by directed vapor beams onto a He-cooled quartz-crystal microbalance (QCM) under ultra-high vacuum. The integrated pore volume (porosity) was calculated by combining the areal mass measured via QCM and thickness measured by UV-visible interferometry. The integrated surface area was indicative by the abundance of incompletely coordinated surface water molecules (H_2O) on the pores, using the O-H dangling bonds (DBs) measured by FT-IR spectroscopy. An *in-situ* Kelvin probe measured film surface potential. A long-distance optical microscope monitored film morphology *in vacuo*. Annealing effects were investigated by heating the film at 1.8 K/min.

The magnitude of the negative surface potential ($|V_s|$) increased linearly with film thickness at rates ($|\Delta V_s/\Delta L|$) that decreased with increasing growth temperature (T_g = 10–110 K), keeping deposition angle at θ = 0° (angle between vapor beam and QCM normal); at T_g = 30 K, the $|\Delta V_s/\Delta L|$ decreased with increasing θ (= 10−75°). ASW porosity showed no dependence on T_g at θ = 0°, but increased significantly with increasing θ. The H_2O DBs decreased/increased with increasing T_g/θ, showing similar trends as the $|\Delta V_s/\Delta L|$. Upon heating, the most striking result was that the DB at ~3720 cm^{-1} (from two-coordinated H_2O) and the $|V_s|$ had similar temperature-dependent evolutions. By correlating all measurements, we propose that the observed intrinsic ASW surface potential results from aligned incompletely-coordinated H_2O on the pore surfaces [2].

The $|V_s|$ decreased abruptly when ASW thickness exceeded a critical value (L_c), and cracks appeared in the optical images of the films. The L_c, ~1–5 µm (T_g = 10–50 K; θ = 0–55°), increased with T_g and θ, suggesting dependences on the microporous structure. We explain such dependences of L_c in the context of Griffith theory and estimate the tensile strength of ASW to be ~25–40 MPa [3].

We acknowledge support from the NASA LASER Program.

[1]Raut et al., *J. Chem. Phys.***127**, 204713 (2007); [2]Bu et al., *J. Chem. Phys.***143**, 074702 (2015); [3]Bu et al., *Appl. Phys. Lett.***109**, 201902 (2016).

9:40am **AS+NS+SA-WeM-6 Speciation and Reactivity of Organic Matter in Uranium Mine Wastes from Laguna- New Mexico: An Application of Surface Sciences in Environmental Systems.**, ***Carmen A. Velasco***, *A Ali,* University of New Mexico; *C Osburn,* North Carolina State University; *K Artyushkova, J Cerrato,* University of New Mexico

The co-occurrence of organic matter and uranium in the Jackpile Morrison formation, New Mexico was investigated using spectroscopy, microscopy, and water chemistry techniques to better understand the effects of organic matter on uranium (U) binding from abandoned U mine wastes. Samples were collected from the Jackpile Mine (JP)- New Mexico. The mean concentration of acid extractable content for mine waste from the JP was 2.61±0.09% U. Results from microprobe mapping suggest that U particles are surrounded by carbon (C) inclusions, while results from XRF analyses showed 2.78% (JP) carbon (C). Loss on ignition (LOI) analysis showed that 19.90±0.95% of organic carbon within the samples. Thermal gravimetric analysis (TGA) show the maximum weight loss between 105°C and 505°C, confirming that change on mass after the LOI is likely due to the loss of organic content of the samples. Analyses using XPS suggest that changes occur on the C binding and U oxidation state after modifying the pH in batch experiments. Emission Matrix (EMM) identified humic-acid and fulvic-acid like components present in the organic matter comprised in the mine waste, which is consistent with the organic functional groups detected by XPS. These findings suggest that uranium minerals are possibly complexed carboxylic functional groups from humic-and fulvic like substances. This study identified the relevance of considering the binding of U and C in mine wastes to better understand U mobilization in the environment.

*This work was awarded the best talk award at the 2018 NMAVS Symposium (Albuquerque-May2018)

11:00am **AS+NS+SA-WeM-10 Optical Constants Measured for Iridium and Samarium by Reflection Electron Energy-loss Spectroscopy Spectra**, ***LiHao Yang***, *H Xu,* University of Science and Technology of China; *A Sulyok, M Menyhard,* Institute for Technical Physics and Materials Science Centre for Energy Research, Hungarian Academy of Sciences (MTA); *K Tokesi,* Institute for Nuclear Research, Hungarian Academy of Sciences (ATOMKI), Hungary; *Z Ding,* University of Science and Technology of China, China

The optical properties, as one of the most important physical properties of materials, arouse a continuous interest of researchers. Accurate measurement of optical data by optical methods in a photon energy range up to 100 eV is still insufficient as special experimental conditions are required during the measurements in vacuum ultraviolet region (20-50 eV). In recent years a well-established technique based on the reflection electron energy loss spectroscopy (REELS) has been developed to obtain optical constants in a rather wide range of electron energy loss. The REELS method does not require a complicated process for preparation of samples and the incident electron energy is usually around a few keV. However, the REELS spectrum usually contains not only bulk excitation but also surface excitation. To remove the surface excitation effect from the REELS spectrum in data analysis, Da et al. [1] have developed a reverse Monte Carlo (RMC) method for the derivation of the energy loss function (ELF) which is directly related to optical constants of a solid.

In the present work, reflection electron energy loss spectra of Ir and Sm were measured at several primary energies ranging from 0.5 keV up to 2 keV and in a wide energy-loss range. Polycrystalline Ir and Sm samples were cleaned by Ar+ ion bombardment. To minimize the surface roughening and damage, glancing incidence angle of 80° with respect the surface normal and low projectile energy of 1 keV were applied with the rotated sample during the sputtering. Cleanliness of surface was checked by continuous detection of main Auger peaks of C and O. A reverse Monte Carlo simulation was performed to extract ELFs of these metals from experimental REELS spectra. All the ELFs have produced REELS spectra in a good agreement within the experimental uncertainty. The reliability of the obtained optical data has been confirmed by applying the Thomas-Ritchie-Kuhn (f-sum rule) and the perfect-screening sum rules (p-sum rule). The good agreement indicates that RMC treats accurately the surface excitation effect which is well removed from the final ELF. Comparisons of our data with other sources from experimental measurements are given.

The work was support by the National Natural Science Foundation of China (No. 11574289) and Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (2nd phase) under Grant No. U1501501.

Reference:

[1] B. Da, Y. Sun, S. F. Mao, Z. M. Zhang, H. Jin, H. Yoshikawa, S. Tanuma, and Z. J. Ding, J. Appl. Phys. 113, 214303 (2013).

11:20am **AS+NS+SA-WeM-11 X-Ray Photoelectron Spectroscopy and Electrical Modeling of Electrowetting on Dielectric Devices**, ***Pinar Aydogan Gokturk,*** Bikent University, Turkey; *B Ulgut, S Suzer,* Bilkent University, Turkey

Electrowetting on dielectrics (EWOD) is a process of changing the contact angle of a droplet sitting on the dielectric covered electrode by the application of external electric field. In majority of the electrowetting experiments reported in the literature, water or aqueous salt solutions are used and ambient medium is either the air, or another immiscible liquid like oil. In this study, for the first time two non-aqueous liquids; (i) polyethylene glycol with an average molecular weight of 600 Da, and (ii) DEME-TFSI ionic liquid, both with low vapor pressure and volatility, are used as droplets in the UHV chamber of an x-ray photoelectron spectrometer (XPS) with traditional electrowetting on dielectric device geometry. With the experimental determination on tracing the electrical potential developments on and around the droplet, using the shifts in the binding energy positions of peaks coming from the liquid and/or the substrate, under imposed AC and DC electrical fields, we are aiming to shed light on the numerous models employed for simulating the electrowetting phenomenon. Additionally, using XPS and incorporating real capacitors and resistors, we mimic and check on the commonly used models used for simulating the electrical behavior of the EWOD systems. Possible and accepted electrical circuit models are also used to simulate the XPS data.

11:40am **AS+NS+SA-WeM-12 Near Ambient Pressure XPS Study of Oxygen Binding to the Surface of Transition Metal-nitrogen-carbon Electrocatalysts for Oxygen Reduction**, *K Artyushkova,* ***Yechuan Chen***, *P Atanassov,* University of New Mexico

The most promising class of platinum group metal-free materials for oxygen reduction reaction (ORR) is based on graphene-like carbon containing nitrogen and transition metal (MNC). It is well established that nitrogen coordination with metal in the carbon network of MNC materials is directly related to ORR activity; however, the exact nature of the active sites is still debated even after over 50 years of research.

The mechanism of oxygen reduction reaction in metal-nitrogen-carbon (MNC) catalysts has been studied by a combination of spectroscopic and theoretical structure-to-activity studies. Using inhibitors that have unique spectral signatures and have strong binding to the active sites allows elucidating the relationship between the chemistry of active sites and its activity.

We will report laboratory-based and near ambient pressure (NAP-XPS) analysis for series of electrocatalysts belonging to Fe-N-carbon families. X-ray photoelectron spectroscopic analysis of the interaction of complexing agents based on phosphonate and *in situ* monitoring of oxygen binding to metal-free active sites provides an important insight into the reaction mechanism. The effect the nitrogen chemistry and the type of iron on the oxygen binding was investigated by NAPXPS under an oxygen environment at operating temperature of the fuel cell. Preferential oxygen binding to different types of nitrogen and iron moieties in presence and absence of inhibitor was followed by spectroscopic changes in high-resolution nitrogen photopeak.

12:00pm **AS+NS+SA-WeM-13 Surface Chemistry of Scandium**, ***Michael Brumbach***, *D Casalnuovo, E Barnat, C Winters, D Robinson Brown, C Snow, A Grillet,* Sandia National Laboratories

Manipulation of metal surface chemistry through vacuum gas dosing has been demonstrated for many years. Additionally, ex situ preparation methods, ion sputtering, and/or in vacuo thermal treatment are all known to change surface properties through oxidation, removal of oxide, change in microstructure, altering contaminants, or other mechanisms. While these studies have been performed for decades, there are few examples of these experiments for pure scandium films. Furthermore, few examples of dosing clean scandium surfaces under vacuum have been published. In this work, scandium films were treated with UV/ozone ex situ cleaning, ion sputtering, and thermal treatment under UHV. These surfaces were then exposed to different gases in the millitorr pressure range for extended periods of time. An optical emission spectrometer was used to monitor the composition of the dosing gas. Surfaces were analyzed before and after dosing. In concert with the gas analyses, the changes in surface chemistry of scandium could be correlated to the dosing species. This work discusses the X-ray photoelectron peak fitting of scandium and the changes in chemistry that can be observed through surface exposures.

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Author Index

Bold page numbers indicate presenter